

# PATENT ABSTRACTS OF JAPAN

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(71)Applicant : SAINT GOBAIN VITRAGE

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(72)Inventor : MINAMI TSUTOMU  
TADANAGA SEIJI

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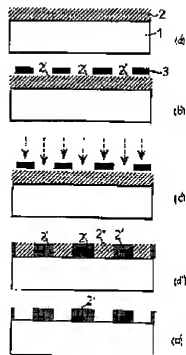
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(54) METHOD FOR BUILDING UP LAYER CONTAINING METALLIC OXIDE AS MAIN COMPONENT

(57)Abstract:

PROBLEM TO BE SOLVED: To directly form a discontinuous layer having prescribed chemical composition in a method for forming the layer through sol-gel.

SOLUTION: The method for accumulating a layer containing metallic oxide as a main component incorporates the following respective processes. (a') Sol is prepared of at least one kind of metallic oxide precursor, at least one kind of a chelating agent and a stabilizer and at least one kind of arbitrary solvent and/or at least one kind of dopant. (b') Sol is built up as a layer 2 on at least a part of one surface of base material. (c') At least a part of sol built as the layer 2 on the base material is irradiated with ultraviolet rays. (d') At least the part of sol irradiated with ultraviolet rays is heat-treated. A continuous layer or a discontinuous layer containing metallic oxide as a main component is built up through sol-gel on the base material, especially the transparent base material. Desirably, the irradiation process (c') and the heat treatment process (d') are alternately performed and repeated by at least one time.



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## CLAIMS

### [Claim(s)]

- [Claim 1] (a) At least one sort of at least one sort of metallic-oxide precursors, a chelating agent, and a stabilizer. A sol is prepared from at least one sort of optional solvents, and/or at least one sort of dopant precursors. (b) Base material (1) A sol is made to deposit as a layer on [ some / at least ] one field. (c) Base material (1) Ultraviolet rays are irradiated at a part of sol [ at least ] made to deposit as a layer upwards. (d) Base material characterized by including each process which heat-treats the part of the sol which irradiated ultraviolet rays at least (1) How to make the continuation layer or discontinuity layer which uses a metallic oxide as a principal component especially deposit through sol gel on a transparency base material.
- [Claim 2] Exposure process (c) The approach according to claim 1 of repeating n times ( $n \geq 1$ ).
- [Claim 3] Heat treatment process (d) The approach according to claim 1 of repeating p times ( $p \geq 1$ ).
- [Claim 4] exposure process (c) Heat treatment process (d) alternation -- carrying out -- an exposure process (c) and heat treatment process (d) Approach given in any 1 term of claims 1-3 repeated once [ at least ].
- [Claim 5] In order to obtain the continuation layer which uses a metallic oxide as a principal component, it is a base material (1). The whole layer of the sol made to deposit upwards is covered, and it is an exposure process (c). Heat treatment process (d) Approach given in any 1 term of claims 1-4 to perform.
- [Claim 6] In order to obtain the etched discontinuous layer which uses a metallic oxide as a principal component, it is an exposure process (c). Or some [ at least ] exposure processes (c) Approach given in any 1 term of claims 1-5 performed alternatively.
- [Claim 7] The method according to claim 6 of performing an alternative exposure process by making a mask intervene between a sol layer and the source of UV irradiation.
- [Claim 8] Exposure process (c) Or some [ at least ] exposure processes (c) Approach including each process which arranges a mask to a sol layer top or the neighborhood, irradiates a sol layer by ultraviolet rays through said mask, removes a mask, and removes the field of the sol layer by which the mask was carried out during the exposure according to claim 6 or 7.
- [Claim 9] An approach given in any 1 term of claims 1-8 as which a metal precursor is chosen from the metal salt, organometallic compound, and metal alkoxide of a halogenide.
- [Claim 10] a metallic oxide -- a precursor --  $\text{SnCl}$  -- two --  $\text{SnCl}$  -- four --  $\text{Sn}$  -- two -- ethylhexanoate --  $\text{Sn}$  -- (OR --) -- four -- or --  $\text{SnR}$  -- ' -- (OR --) -- four (R and R' is a carbon content radical) -- a gestalt -- tin oxide -- a precursor -- it is -- being according to claim 9 -- an approach .
- [Claim 11] The organic compound with which a chelating agent/stabilizer has a ketone group and/or an ester group especially 2, 4-2,4-pentanedione, 1-phenyl - 1 Three - Approach given in any 1 term of claims 1-10 chosen from a butanedione and beta-diketone group of ethyl acetoacetate.
- [Claim 12] Organic-acid fluoride and  $\text{SbCl}_3$  whose dopant precursor is Or  $\text{SbCl}_5$  Approach given in any 1 term of claims 1-11 chosen from a metal halogenide [ like ]. [ like trifluoroacetic acid ]
- [Claim 13] An approach given in any 1 term of claims 1-12 whose solvents are the organic substance which has an alcoholic radical like ethanol or isopropanol especially, a sodium hydroxide, or an inorganic substance like aqueous ammonia.
- [Claim 14] The approach according to claim 7 or 8 of being the photo mask which the mask used resin as the principal component and was made to deposit with photolithography, or the mask made to deposit on a glass base material.
- [Claim 15] Sol (b) Approach given in any 1 term of claims 1-14 deposited with spin coating, DIP coating, stratified coating, or a spray.
- [Claim 16] Exposure process (c) It is a 250-360nm electromagnetic wave to a sol layer preferably 100 - 200 mW/cm<sup>2</sup> Approach given in any 1 term of claims 1-15 used by reinforcement.
- [Claim 17] Heat treatment (d) It is an approach given in any 1 term of claims 1-16 especially performed at 200-500 degrees C at least 100 degrees C.
- [Claim 18] the continuation layer or discontinuity etching layer (2) containing a metallic oxide it is -- especially

the approach of a publication .

[Claim 19] Base material according to claim 18 which is the base material which uses as a principal component the transparent base material with which a base material consists of glass or an organic polymer, a ceramic, or a glassiness ceramic ingredient, or a base material which uses silicon as a principal component (1) .

[Claim 20] the continuation layer or discontinuity etching layer (2) obtained through sol gel it has been arranged downward — especially —  $\text{TiO}_2$   $\text{ZrO}_2$  etc. — base material (1) according to claim 18 or 19 which consists of a metallic oxide or the oxide of silicon, acid carbide, an acid nitride, a nitride, etc. and which was equipped with another thin layer at least .

[Claim 21] Use for making a layer deposit on the base material which uses as a principal component the transparent base material which is use of the deposition approach of a publication and becomes any 1 term of claims 1-17 from glass or an organic polymer, a ceramic, or a glassiness ceramic ingredient, or the base material which uses silicon as a principal component.

[Claim 22] It is use of the deposition approach given in any 1 term of claims 1-17 on which the continuation layer or discontinuity etching layer which uses as a principal component the tin oxide doped by using tin oxide as a principal component is made to deposit. The tin oxide which was doped with a halogen like a fluorine, or ( $\text{F:SnO}_2$ ) was especially doped with the periodic table Va group metal, Use for making the layer which uses as a principal component the indium oxide (ITO) doped with doping tin oxide ( $\text{As:SnO}_2$ ) or tin deposit with the tin oxide ( $\text{As:SnO}_2$ ) doped with arsenic, and antimony.

[Claim 23] Manufacture of manufacture of a conductive element / electrode, or antistatic coating especially a heating type aperture, or a type aperture with a built-in antenna, manufacture of the radiation screen of a flat screen stencil, for example, a plasma screen, or a touch screen or use especially in photovoltaic cell industry in electronics industry. [ in / it is use of the deposition approach given in any 1 term of claims 1-17, or use of a base material given in any 1 term of claims 18-20, and / a glass manufacture ]

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## DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the approach of making the layer which uses a metallic oxide as a principal component, and the layer which uses as a principal component in more detail the metallic oxide which has some conductivity at least depositing. Although this invention more specifically originates in the property and thickness of a proper and it is related to a transparent layer, this invention does not eliminate an opaque layer here.

[0002]

[Description of the Prior Art] Especially this invention relates to making such a layer deposit on glass or the transparency base material of the base material of the polymer organic substance. Many products using a transparency base material are continuation coatings equipped with the layer which actually needs such a layer, for example, has the conductivity of an antistatic function and a low, or a heating function, or are the gestalten of discontinuity coating etched into the predetermined pattern. These are base materials which need the conductive element / electrode which has uniform high degree of accuracy (resolution) or it excelled, for example, and, specifically, the electrode of the glass of a flat screen-stencil radiation screen, the electrode of a photovoltaic cell, the conductive element of a heating type aperture, a type aperture with a built-in antenna, conductive coating that has the electric shielding function of an electromagnetic wave are mentioned.

[0003] About the such type layer, many deposition techniques are already examined. For example, manufacture of the layer which uses the metallic oxide and silicon oxide by the so-called "sol gel" method as a principal component is known. This manufacture principle consists of forming the oxide of network structure by being similar to composition of an organic polymer, carrying out the polymerization of a compound precursor like a metal alkoxide in a solution by hydrolysis, and subsequently carrying out condensation gradually with ambient temperature. By heat treatment in a final process, the layer of the obtained oxide is dried and eburnation is carried out.

[0004] This approach is advantageous at the point that adaptability is in various kinds of applications, and it is very easy in operation. However, it also has many constraint. For example, the performance characteristics of the always optimal layer cannot necessarily be obtained with predetermined chemical composition. Moreover, even if a discontinuous patterned layer is now required, it is necessary to pass for a continuation layer to be obtained but to etch it according to a separate process.

[0005] Therefore, the purpose of this invention is offering the improving method which forms the layer which uses a metallic oxide as a principal component, and solving these problems with a sol gel process, and is making it possible to obtain the layer of the higher engine performance also in any of continuation or discontinuity.

[0006]

[The means for solving a technical problem and an effect of the invention] Especially the approach of this invention makes the continuation layer or discontinuity layer which uses a metallic oxide as a principal component deposit on a transparency type base material with a sol gel process first. This approach includes the following process at least.

a) At least one sort of metallic-oxide precursors, at least one sort of chelating agents/stabilizers, A sol is prepared from at least one sort of optional solvents, and/or at least one sort of dopant precursors. (b) one field of a base material — a sol is deposited as a layer in part at least — making — (c) a part of sol [ at least ] made to deposit as a layer on a base material — ultraviolet rays — irradiating — (d) the sol which irradiated ultraviolet rays — the part is heat-treated at least.

[0007] Please understand the vocabulary "discontinuity" layer in this invention to be that to which the pattern of a discontinuous gestalt which leaves a continuation layer and is usually acquired by etching carries out the designation of the layer directly obtained by the predetermined pattern. Since it is brief, using the vocabulary in the field of a sol gel process, it sets at each process of the above-mentioned process, and it is indicated that a "sol" is created and used. Here, probably, it will be clear to this contractor that the sol's [ after making it

by the reaction between the various chemicals contained in a sol.

[0008] It sets in one mode which carries out the process of this invention, and is an exposure process (c). It is repeated n times ( $n \geq 1$ ). It sets in another mode which carries out the process of this invention, and is a heat treatment process (d). It is repeated p times ( $p \geq 1$ ). In a desirable mode, an exposure process and a heat treatment process are carried out one by one, and at least 1 time of an exposure process (c) is repeated. At least 1 time of heat treatment process (d) (it does not eliminate that another down stream processing intervenes between an exposure process and a heat treatment process.) Moreover, 1st exposure process (c) A heat treatment process can also be performed in front.

[0009] As a matter of fact, it is the process (a) of the process of this invention. (b) And (d) Generally a base is looked at by the standard sol gel process, and this is because it is based on deposition of the sol by which this process is converted into gel and eburation is carried out to a final oxide by heat treatment. That is, it finds out that it improves the condition that a layer is created that this invention inserts the process of the sol layer exposure by ultraviolet rays into a process for useful purpose, and this is considered for ultraviolet rays to promote destabilization of the metal precursor contained in a sol, and the complex generated between a stabilizer/chelating agent. It is thought that this destabilization brings about the preliminary polymerization by which the metallic-oxide precursor was controlled.

[0010] Therefore, the unexpected effectiveness of these ultraviolet rays can be efficiently employed in the range of this invention in the two different methods of pulling out the effectiveness especially acquired from it. That is, when to obtain the continuation layer which uses a metallic oxide as a principal component is desired, it is a UV irradiation process (c) to the whole sol layer. Heat treatment process (d) It can carry out. Therefore, by ultraviolet rays, it is very useful at the point that the polymerization of a layer can be controlled more appropriately, and, in a certain case at least, the specific last property of a layer can be improved about the given chemical composition of a sol, and it can especially be made conductivity more. Moreover, it is also found out that it can act on the crystallization temperature of an oxide, without exposure to ultraviolet rays complicating the formation process of a layer too much.

[0011] When to obtain the discontinuity layer which has a given pattern is desired, ultraviolet-rays exposure makes it possible to obtain such a layer without etching of a layer directly after that. this -- process (c) between -- or process (c) At least in a part, it is because it is found out that it is possible to carry out UV irradiation of the field equivalent to a base material field to make it deposit not the whole layer but an oxide on alternatively. That is, while the polymerization of the sol layer of a partial field can be carried out preparatorily, in the field which is not irradiated, there is a metallic-oxide precursor to stabilization raw, and it is kept fundamental with the gestalt of a complex. The non-irradiating field of a sol is easily [ for a rate ] removable, and only the field irradiated preparatorily remains, and this field is fully thermally hardened by the usual method so that the discontinuity layer which has the request pattern defined by irradiating a sol alternatively may be obtained, so that it may specifically explain below.

[0012] Various methods can perform this alternative exposure. making it collide to the opposite side in the case of the base material which move the source of ultraviolet rays relatively to a base material, and ultraviolet rays are made to collide with a base material in respect of the sol layer having been given for example, or essentially consists of a diactinism ingredient, although not limited -- having said -- making -- electromagnetism -- the source of ultraviolet rays which can carry out the channeling of the line can be used.

[0013] another method of performing an alternative exposure makes a mask intervene between a sol layer and the source of UV irradiation -- it is -- the same -- the top face of the sol layer on a base material -- or in the case of the base material which consists of a diactinism ingredient, the opposite side is irradiated. A mask turns the source of ultraviolet rays appropriately to a mask so that it may be held at a certain distance and ultraviolet rays may be irradiated like a request on a sol layer from a sol layer. It can follow, for example, can also cover with the mask on a diactinism base material like a glass plate, and this can also be arranged so that it may arrange on a sol layer in a desired distance or the non-mask side of a glass base material may contact a sol layer.

[0014] Moreover, as for a mask, it is desirable to carry out preheating (for example, very moderate heating) of the sol layer a little so that a sol layer can also be made to contact directly and sufficient viscosity to support a mask equally in this case may be given. In short, an alternative UV irradiation process can include the following small process (it takes into consideration whether it is \*\*\*\*\* from which it is here and the sol has already obtained the workability of gel).

[0015] \*\* On the 2nd glass base material arranged on a sol layer The gel layer field by which the mask was carried out during the \*\* exposure which removes the \*\* mask which irradiates a sol layer alternatively by ultraviolet rays through the \*\* mask which adjoins a sol layer and prepares a mask is removed (when two or more alternative exposure processes are prepared in a process, small process \*\* and/or small process \*\*). at least one process -- not in each process but in a final process, it can especially carry out. Various methods can remove a mask and specifically, it is decided by the chemical property, the easiest method

is directly deposited on the gel layer — if it becomes — mechanical — \*\*\*\* — stripping — — it is removing. What is necessary is just to only remove the another base material, if it has deposited on another base material arranged on a gel layer.

[0016] Moreover, the removal of a non-irradiating field by which the mask was carried out is also various methods, and can be performed especially chemically, namely, it is based on the suitable thing generally melted with the solvent or mixed solvent of the organic substance. Moreover, it can also carry out by dipping and washing a base material in a solvent bath, or carrying out the spray of the solvent to a layer etc. Since the polymerization is advancing far, the exposure field itself can be borne at this removal processing.

[0017] Next, the process which prepares the sol by this invention explains usable various chemicals (not limited). As for a metallic-oxide precursor, it is advantageous to choose from the metal salt, organometallic compound, and metal alkoxide of a type of a halogenide. Since this invention is specifically related to generation of the layer which uses an oxide as a principal component,  $\text{SnCl}_2$ ,  $\text{SnCl}_4$ ,  $\text{Sn}-2$ -ethylhexanoate, and  $\text{Sn}_4(\text{OR})\text{SnR}'(\text{OR})_4$  An alkoxide etc. is mentioned. R and R' the alkyl group of the straight chain which may be the same, may be different, for example, has carbon of 1-6 including carbon, or a branch separation chain — it is — tin tetra-isopropoxide ( $\text{O}-i\text{-Pr}$ )  $\text{Sn}_4$  etc. — it is .

[0018] A chelating agent/stabilizer is preferably chosen from the organic compound which has a ketone and/or an ester group, and the compound belonging to beta-diketone group. For example, 2, 4-2,4-pentanedione, 1-phenyl - 1 Three - A butanedione and ethyl acetoacetate are mentioned. If a dopant does not exist, the layer of a metallic oxide will be insulation, and if behavior is carried out as dielectric matter or oxygen depletion exists especially in an oxide grid, it will be conductivity a little. When it is desirable to guarantee the conductivity of high level to a rate here, it is required for a sol by adding a dopant precursor to dope an oxide. This dopant can be a halogen and a halogen content precursor can be halogenated trifluoroacetic acid of the organic acid by which especially fluoride was carried out, for example. A dopant can also be a replaceable metal about the basis metal of the metallic oxide to generate. When to dope the layer of tin oxide is desired, a suitable dopant metal can be As, Sb, etc. which are chosen from a periodic table Va group, and the precursor can be the gestalt of a metal halogenide (for example,  $\text{SbCl}_3$  or  $\text{SbCl}_5$ ).

[0019] The solvent by request is desirable alcohol like ethanol or isopropanol. Moreover, it can also be an inorganic system solvent like a sodium hydroxide or aqueous ammonia. In the mode which uses a mask for performing alternative UV irradiation of a sol layer, a thing [ like the photo mask deposited with the photolithography of a well-known method, for example ] whose mask is and which uses resin as a principal component is chosen. Moreover, a mask can also be deposited on a glass base material etc. as mentioned above.

[0020] Sol deposition process (b) For example, the thickness of 5-1000nm and the well-known technique of the arbitration on which a sol layer with a uniform thickness of at least 10nm can be made to deposit preferably can perform. For example, a sol can be made to deposit with the technique which spin coating, DIP coating, thin layer coating, and a spray are mentioned, and is called roller coating and meniscus coating.

[0021] UV irradiation process (c) especially — the optical reinforcement on a sol layer — about 150 mW/cm<sup>2</sup> — especially — 100 - 200 mW/cm<sup>2</sup> it is — it is desirable to divide and to use especially about 300nm of wavelength of 250-360nm. Heat treatment process (d) It is common to carry [ at least 100-degree C ] out at 200-550 degrees C especially. Especially temperature should be adjusted in the range corresponding to the chemical property of a base material, when a base material consists of glass or an organic polymer.

[0022] Moreover, this invention relates to applying this process to deposition of the layer on the base material which consists of the transparency base material which consists of glass or an organic polymer, a ceramic, or a glassiness ceramic, or a silicon base material. Moreover, this invention is F:SnO<sub>2</sub>, Sb:SnO<sub>2</sub>, and As:SnO<sub>2</sub>. It is related with applying this process to continuation of the indium oxide which doped the tin oxide [ like ] doped optionally or tin, or deposition of a discontinuity layer. It has conductivity and is SnO<sub>2</sub>. It turns out that this invention is especially suitable for etching of a layer used as a principal component, or the creation of a layer by which pattern formation was carried out with the sufficient result. Here, it has been thought conventionally that especially these layers are difficult to etch using the usual chemical etching technique since it is known that there is chemical resistance. Here, this invention is discontinuous SnO<sub>2</sub>. It is related with the approach of obtaining a principal component layer directly. Generally especially these layers have 5-1000nm of thickness of at least 10nm.

[0023] Furthermore, the purpose of this invention is related with applying this process to manufacture of the electrode / conductive element in various fields. This field is glass industry and an automobile, the aircraft, etc. can form a conductive network in the aperture and the type aperture with a built-in antenna which are heated according to the Joule effect. Moreover, the approach of this invention can also be used in order to form coating which has the function which covers the electromagnetic wave of the aperture of the building in which it is located near the airport. Moreover, this field can also be photovoltaic cell industry. furthermore, the screen which this field can also be electronic industry and is called the radiation screen of a flat screen stencil and a

of the type of arbritration which can especially irradiate the light, and can penetrate or can be emitted or tooth back of an electromagnetic wave more widely.

[0024] Moreover, this invention relates to the above-mentioned base material characterized by the continuation layer or discontinuity etching layer obtained through the sol gel process including the metallic oxide according to the above-mentioned process. This base material can also have the additional thin film. According to the desirable mode, especially this base material has one thin film which consists of dielectric ingredients (for example, the metallic oxide of  $\text{TiO}_2$ ,  $\text{ZrO}_2$ , etc., the oxide of silicon, acid carbide, an acid nitride, a nitride, etc.) and which will be rubbed if few. This thin film is located under the layer by this invention. This lower layer (sub-layer) Although obtaining with a sol gel process is desirable, other depositing methods are not eliminated (deposition using vacuums, such as a cathode sputtering and CVD). 10-150nm, especially this can have the geometric-like thickness of 15-80nm or 40-70nm, and can do here where various functions are achieved according to the chemical property and its thickness (the barrier to the alkali element from a glass base material, layer which has optical or a fixed operation). This may be etched although it is desirable that it is continuation.

[0025] Next, it is shown in an accompanying drawing and the example which is not limited explains this invention in more detail.

[0026]

[Embodiment of the Invention] For these, the base material used in the following detailed explanation is a standard silica soda lime float glass base material, the alkali-free-glass base material (lot number 7059) of Corning, Inc. to sale, or  $\text{SiO}_2$ , although each example shows. Or it is a silicon base material. The other suitable glass constituents especially for the application of the electronics field are indicated by WO 96/11887, WO 98/40320, and EP-854117.

[0027] With regards to deposition of the layer to which any example uses an oxide as a principal component, as each example was shown, or the oxide is not doped, it is doped with a fluorine or antimony and it has the thickness of about 100nm (10-1000nm). The schematic diagram shows the main processes of two sol gel deposition processes by this invention to drawing 1 and drawing 2, and drawing 2 is related with deposition of a discontinuity layer by drawing 1 about deposition of a continuation layer.

[0028] It is related with drawing 1 and is the 1st process (a). Although it sets, the layer of the fixed homogeneity of a sol 2 is given to a base material 1 and the presentation is shown in the example, at least one sort of chelating agents for preventing at least one sort of tin oxide precursors and the reaction which is made to stabilize it and cannot control between metallic-oxide precursor molecules quickly too much are included. A sol has the workability of gel by desiccation and a gel layer is hardened.

[0029] The 1st process (b) It sets, the whole layer 2 is exposed to the exposure of ultraviolet rays, a complex is made unstable by a certain kind of photolysis, and a preliminary polymerization with the quick layer by the chain reaction between metallic-oxide precursors is brought about. In this way, layer 2' which carried out the polymerization is a process (c). The eburnation is made to complete, as it sets, heat treatment is presented and only the structure of an inorganic metallic oxide is held.

[0030] About drawing 2, the layer which uses tin oxide as a principal component has a given pattern, and is obtained directly. A process (a') makes the fixed layer of a sol 2 deposit on a base material 1 like the point. Subsequently to a layer 2, with photolithography, a process (b') makes the resinous principle mask 3 which contacts deposit, and adjusts the viscosity by the suitable method beforehand.

[0031] A process (c') irradiates ultraviolet rays at a layer 2 and a mask 3. In order that a mask 3 may intercept ultraviolet rays, the "preliminary polymerization" under ultraviolet rays and an exposure operation is presented only with field 2' in fact. By stripping off, a mask 3 is removed and, as for a process (d'), field 2'' of the layer 2 to which is followed and eburnation and a preliminary polymerization are not carried out like field 2' which is not irradiated in this way is exposed.

[0032] A process (e') can remove field 2'' which is not irradiated, and this can perform it by only washing a base material 1 with the sodium-hydroxide solution and aqueous ammonia of the alcohol of a suitable organic solvent, or an inorganic solvent. A final process (not shown) heat-treats field 2' which remains, makes the eburnation complete, and is used as a metallic oxide. The etched layer which has by this a pattern corresponding to the pattern given with a mask 3 is obtained directly.

[0033] The sol which contains a tin tetrapod iso PUROI rate as a metallic-oxide precursor is used for Examples 1-5 of the first series. The following method performs preparation of this sol. A tin tetrapod iso PUROI rate ( $\text{Sn}_4(\text{O}-i\text{-Pr})$ ) is melted to the solvent of isopropanol  $i\text{-PrOH}$ . Add the chelating agent of a tin oxide precursor in the solution, namely, an embodiment is embraced. 2 called an acetylacetone (AcAc) as shown in drawing 3 a, 4-2,4-pentanedione, 1-phenyl called a benzoylacetone (BzAc) as shown in drawing 3 b - 1 Three - A butanedione is added. Subsequently In order to obtain a desired sol, isopropanol and water  $\text{H}_2\text{O}$  are added and the viscosity of a sol is adjusted.

[0034] A chelating agent makes a tin tetrapod iso PUROI rate stability. That is, an acetylacetone forms

association between tin and tin by the substitution reaction of the alkoxy group of a tin alkoxide, and forms the complex shown in drawing 3. the following table 1 -- five examples -- each -- it attaches and the exact presentation (mol unit) of the sol per one-mol tin oxide precursor is shown.

[0035]

[Table 1]

	Sn(O-iPr) <sub>4</sub>	i-PrOH	AcAc	BzAc	H <sub>2</sub> O
例 1	1	30	1		
例 2	1	30	2		
例 3	1	30	1		2
例 4	1	30	2		2
例 5	1	50		1	2

[0036] Examples 6-9 of the 2nd series are tin dichloride SnCl<sub>2</sub> as a tin oxide precursor. The included sol is used. The following method performed preparation of this sol. The mixture of SnCl<sub>2</sub> / acetylacetone is prepared by 1/20 of mole ratios about Examples 6-9. Subsequently, nothing adds or (Example 6) a dopant is added (Examples 7, 8, and 9). Namely, a dopant / SnCl<sub>2</sub> A mole ratio is set to 0.1. In Example 7 CF<sub>3</sub>COOH, At Example 8, it is SbCl<sub>5</sub> in SbCl<sub>3</sub> and Example 9. It adds, is related with Example 10 and is SnCl<sub>2</sub>. The mixture of ethanol is prepared by 1/20 of mole ratios, and, subsequently it is the dopant SbCl<sub>3</sub> in ethanol. It added (the mole ratio of SbCl<sub>3</sub> / SnCl<sub>2</sub> is 0.06). To the last, it is an acetylacetone in ETARURU AcAc/SnCl<sub>2</sub> It added by the mole ratio 0.4.

[0037] The sol prepared in Examples 1-5 was used as follows. The used base material is SiO<sub>2</sub> which has a dimension with a thickness of 1mm by 20mmx20mm. Are a base material and the glass ejection rate of a sol bath is carried out for each five sol in about 0.20 or 0.4mm/second using a DIP coating method. It is made to deposit as a thin layer with a thickness of about 20-500nm on glass, and five base materials to which five layers of the sol which serves as workability of gel quickly were given are created. Subsequently It is five glass on the gel film About 150 mW/cm<sup>2</sup> By optical reinforcement, it put to the exposure of the ultraviolet rays which have the wavelength of 250-360nm, and subsequently, in order to make gel convert five glass into the layer of tin oxide completely, it heat-treated at the temperature of 100-600 degrees C.

[0038] The reinforcement of about 335nm absorption band (pi-pi\* of the complex generated by Sn (O-i-Pr)<sub>4</sub> and BzAc it corresponds to transition) which shows the light of a gel layer in process and change of absorption of ultraviolet rays which expose the gel layer of Example 5 to ultraviolet rays, namely, is observed first decreases greatly, and drawing 4 disappears completely after the exposure it is [ exposure ] 360 seconds. Thus, by ultraviolet rays, a complex is destabilized greatly and disappears in several minutes. The thickness of gel falls about 30% in the case of UV irradiation.

[0039] The following table 2 is SnO<sub>2</sub> obtained as a function of temperature (degree C) used for heat-treating the final process in the case of Example 3. The value of conductivity [ of the S/cm unit of a layer ] sigma (uv) is shown. (Example 3' used the above-mentioned Corning glass base material, and also the same method as Example 3 performed it.)

[0040]

[Table 2]

例 3	T	$\sigma$
	100	$0.9 \times 10^{-8}$
	200	$5.0 \times 10^{-5}$
	300	$2.0 \times 10^{-3}$
	400	$7.0 \times 10^{-2}$
	500	$1.8 \times 10^0$
	600	$4.4 \times 10^0$
例 3'	450	$5.0 \times 10^1$

[0041] In example 1a - example 5a, although the same sol as Examples 1-5 was used, the silicon base material was used. Before putting gel to ultraviolet rays, it was made to harden slightly and the glass base material which covered the mask was made to deposit on those front faces by drying gel for several minutes at about 50-100 degrees C. The mask is sold by the Edmond scientific company by the name of article of "the test target USAF1951." This is the gestalt of a parallel band from which width of face was mutually separated in the



reach sufficient viscosity of about 105 Pa-s.) The layer reproducing the pattern of the mask which has a very high precision was obtained covering the thickness of about 100nm. Being able to see this to drawing 5, this drawing shows the profile of one layer of these examples which was measured in surface pro FIRO meter and which was attached and obtained.

[0042] The sol prepared in Examples 6-9 was used as follows. The used base material is Corning glass mentioned above, and a base material is made to deposit one layer of each sol in spin coating. About Examples 1-5 UV irradiation is beforehand performed over 10 minutes. Subsequently as mentioned above Heat treatment for about 5 minutes was performed at the temperature of 350-550 degrees C, UV irradiation and heat treatment were carried out by turns, this was repeated 4 times and it considered as the end by heat treatment at the above-mentioned temperature for 1 hour, and finally, two silver electrodes were used and the resistivity of the last layer was measured.

[0043] Table 3 summarizes the property of a layer, heat-treatment-temperature T (degree C), and resistivity (ohm-cm) about each example.

[0044]

[Table 3]

	T	350	400	450	500	550
例 6	SnO <sub>2</sub>	1.2	$2.6 \times 10^{-2}$	$2.0 \times 10^{-2}$	$2.3 \times 10^{-2}$	
例 7	SnO <sub>2</sub> (F)		2.4	$7.0 \times 10^{-2}$	$2.9 \times 10^{-2}$	$2.5 \times 10^{-2}$
例 8	SnO <sub>2</sub> (Sb <sup>+++</sup> )			$1.1 \times 10^{-1}$	$3.5 \times 10^{-2}$	$6.8 \times 10^{-2}$
例 9	SnO <sub>2</sub> (Sb <sup>+</sup> )			5.1	$1.6 \times 10^{-2}$	$7.0 \times 10^{-2}$

[0045] The sol prepared in Example 10 was made to deposit on a Corning type glass base material by heat treatment of a short time after three spin coating and each deposition. Subsequently, final heat treatment of 1 hour was presented as mentioned above at the UV irradiation for 10 minutes, and the temperature of 350-550 degrees C. The obtained layer has the resistivity of  $1.5 \times 10^{-2} - 8 \times 10^{-3}$  ohm-cm, this value was decided by heat treatment temperature, and the minimum resistivity was obtained at about 450 degrees C.

[0046] In order to obtain the layer by which pattern formation was carried out, the mask of Examples 1a-5a can also perform Examples 6-10. As a conclusion, this invention offers new this invention including the ultraviolet treatment which forms a layer through a sol gel process, and this approach is SnO2. Although the layer used as a principal component is very firm and has chemical resistance, it enables etching on manufacture and the spot with the sufficient result.

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[Translation done.]